

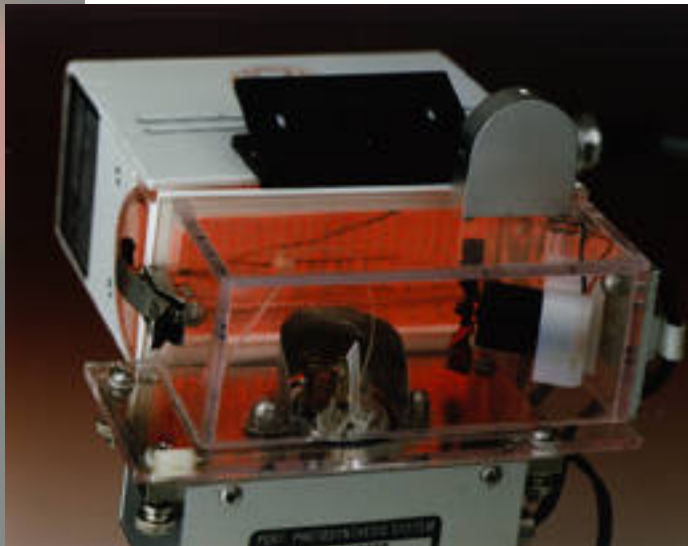
# Elevated CO<sub>2</sub> Exposure and Tree Growth

**T**HE global average climate has been relatively stable for several thousand years. However, human activities in the industrial and developing nations now threaten to cause unprecedented, rapid, and persistent climatic changes due, in large part, to changes in the composition of the Earth's atmosphere. For example, the burning of coal, oil, gas, and forests have increased the atmospheric concentration of carbon dioxide (CO<sub>2</sub>) by 25% since preindustrial times. Over approximately the same period, global average temperatures have increased by about 0.5°C, suggesting an enhanced greenhouse effect. Greenhouse gases in the atmosphere act to trap the Earth's long-wave or infrared radiation, raising the Earth's average surface temperature.

Current global atmospheric and climate models show important disagreements in their predictions. Nevertheless, projected increases in CO<sub>2</sub> (atmospheric levels are expected to double in the next century) and associated climate changes (such as warming and increased water vapor in the atmosphere) could substantially affect forests around the world. Because it is not practical to test the response of all forest habitats and species to elevated CO<sub>2</sub>, we are investigating two diverse forest species so that we can develop broad generalizations.

To assess the differential and variable effects of elevated CO<sub>2</sub> within the forest, we chose two important species of conifer, *Taxus brevifolia* and *Pinus ponderosa*. These two conifers have pronounced differences in morphology and physiology. *P. ponderosa* is an economically important, shade-intolerant, canopy-dominant conifer with a range extending from the

*Photosynthetic measuring system. This apparatus, which contains red light-emitting diodes (LEDs) as a cool source of light, is used to measure CO<sub>2</sub> uptake by a leaf. At left is a close-up view of the needles with the LEDs shown in the background.*



California coast to the Rocky Mountains and from Canada to Mexico. Climate changes affecting *P. ponderosa* could result in substantial ecological and economic impacts. *T. brevifolia*, commonly known as the Pacific Yew, is the tree from which the medicinal compound taxol is extracted. Because this conifer has higher internal limits to CO<sub>2</sub> uptake and possible limits in exporting carbon from the needles, higher levels of atmospheric CO<sub>2</sub> could be harmful to this species.

Last year, we completed the construction of an elevated CO<sub>2</sub> exposure facility at LLNL and began to gather baseline measurements. We have collected about 6000 one-year-old and four-year-old seedlings from diverse regions of California. The seedlings come from 89 genetically identified sources that can be grouped into three broad categories. In full siblings, both the male and female components are known; in half siblings, the female component is known; in open-pollinated seedlings, neither component is known.

In April 1993, we began our 3-year-long exposures of the seedlings to either ambient conditions or to elevated levels of CO<sub>2</sub> (ambient + 175 ppm CO<sub>2</sub>, or ambient + 350 ppm CO<sub>2</sub>). Multidisciplinary measurements are being collected at 3-month intervals. These measurements are giving us information on how enriched CO<sub>2</sub> affects the physiological, biochemical,

and morphological processes that are interrelated through an underlying source-sink control mechanism. As the name suggests, source-sink mechanisms in the context of our work are those that affect where a plant's carbon comes from and where the carbon ends up. For example, the principal carbon source for plants is photosynthesis, which involves the uptake and incorporation of carbon from the atmosphere. Any change in temperature or CO<sub>2</sub> will affect photosynthesis, which, in turn, affects the carbon source.

Our early results show variable growth responses in the *P. ponderosa* seedlings we have begun to assess. For example, the stem diameter of seedlings exposed to elevated CO<sub>2</sub> levels (specifically, the +350 ppm group) increased relative to the stem diameter of the ambient group, but the increases varied from 2.6% to 22.4% when these data were gathered in late 1993. On the other hand, elevated CO<sub>2</sub> resulted in a decrease in quantum yield, which is a measure of the absorption of CO<sub>2</sub> per unit of light. Once again, the responses varied among the seedling sources, ranging from -2.1% to -23.2% compared to the ambient group as of February 1994. The source trees that had the best growth throughout the study period also had the least reduction in quantum yield due to elevated CO<sub>2</sub>.

We are also measuring other physiological and biochemical changes. For example, observed decreases in the pigmentation of *P. ponderosa* due to elevated CO<sub>2</sub> are not associated with any particular family of this species. Our investigation of leaf ultrastructure, in contrast, shows differences due to family. The best growth performer shows no starch buildup in the chloroplasts, whereas the poorest growth performer shows starch buildup. (Chloroplasts are plant structures that contain chlorophyll pigments and function in photosynthesis.) The differences in starch levels were most evident during nondormant periods. Our enzymatic assays are showing that those families of seedlings with better growth at higher levels of CO<sub>2</sub> also had higher enzymatic activity.

Although it is clearly too early to draw any final conclusions, our work suggests that changes in CO<sub>2</sub> levels have complex and variable effects on plant physiology and morphology, some of which arise from a genetic component (intraspecific variability). In the coming year, we will continue to expose seedlings to elevated levels of CO<sub>2</sub> and collect multidisciplinary measurements. We also plan to expand the number of enzymatic assays we will perform. We will integrate



*The elevated CO<sub>2</sub> exposure facility at LLNL is allowing us to study the differences between conifer seedlings growing under ambient conditions and those growing under elevated levels of CO<sub>2</sub>.*

these measurements through statistical models and determine which families are responding best to the elevated exposures of atmospheric CO<sub>2</sub>. Over the longer term, our work may ultimately allow us to define long-range predictive parameters that could be used in impact assessment and forest management.

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# Meniscus Coating

**N**EW optical coating materials and laser technologies have created a need for large optics with uniform, ultrathin coatings that are applied from liquid solutions. Such devices are used, for example, in high-power laser systems at LLNL and elsewhere. To manufacture these optics, coatings a micron in thickness or less need to be deposited with extreme uniformity—to within a few percent—across the entire clear aperture, which can be on the order of a square meter in size.

Micron- and submicron-scale films have been traditionally applied from liquid solutions by spin coating or dip coating. However, spin coating massive optics at the high rates needed to achieve a uniform film is not practical and wastes the coating fluid. Dip coating requires large volumes of expensive coating fluids and risks intercontamination of materials in a multilayer application.

We have been investigating an alternative process known as meniscus coating. (A “meniscus” is the curved free surface of a liquid near the walls of a vessel.) Although the process has had limited use in industry for several years, it has only recently been well characterized and optimized.

The figure shows the essential features of our meniscus coating process. Coating fluid from a reservoir is forced through a filter and into the ends of a slotted applicator tube. The fluid flows up out of the slot and down over the outside of the tube to drain back into the reservoir. A surface to be coated is placed a fraction of a millimeter above the applicator tube, which moves relative to the substrate. When the liquid layer atop the tube intersects the substrate, fluid attaches to the substrate surface by capillary forces. As the relative motion continues, a thin film becomes entrained on the substrate.

The fluid dynamics that control the entrained film thickness are almost identical to those for dip coating. The film thickness is proportional to the  $2/3$  power of the translation rate of the applicator (identified as  $V$  in the

*Schematic cross section of our meniscus coating device. Coating fluid is pumped through a filter and forced through an applicator tube's longitudinal slot. Fluid attaches to the substrate by capillary forces, and a thin film is entrained on the surface. The result is extremely uniform coatings on planar substrates of nearly any size.*

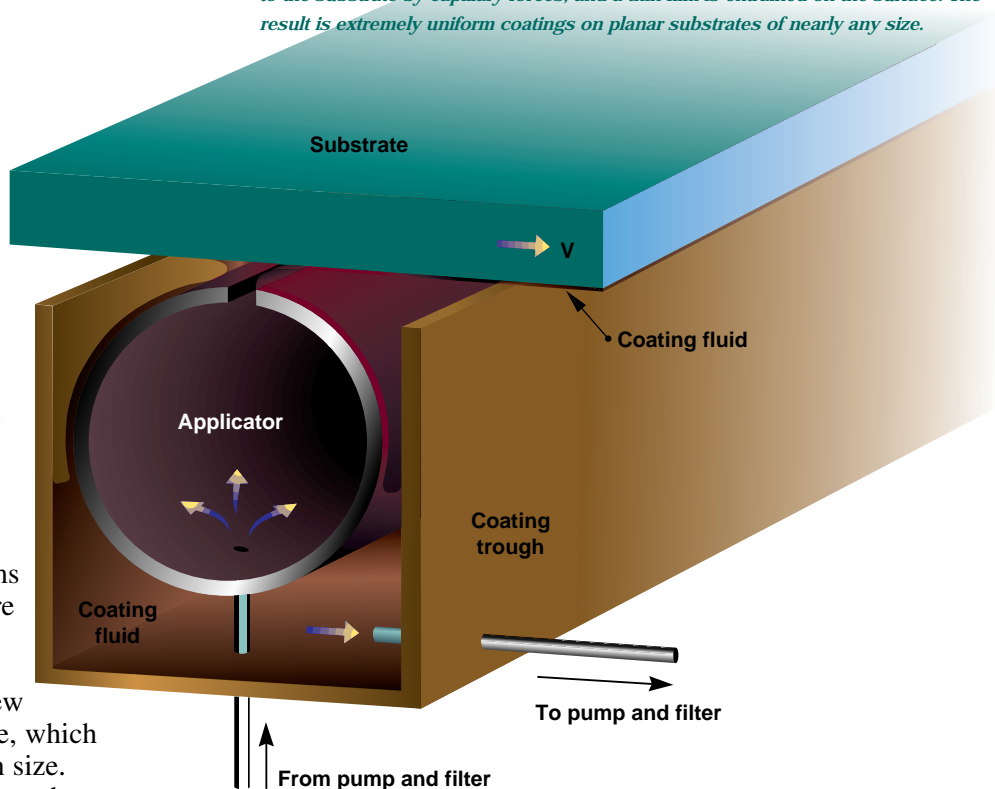


figure above). Controlling the way the film dries after it is applied is an essential step in ensuring film uniformity.

We have applied coatings 0.1 to 3.5  $\mu\text{m}$  thick and with typical uniformities of  $\pm 2.5\%$ . A distinct advantage of meniscus coating is its efficient use of the fluids. Our process provides nearly 100% utilization of a coating fluid, and with in-line filtration, its lifetime is extremely long. We have used the same 700-ml charge of fluid for over 2 months of continuous recirculation to coat dozens of substrates with no loss in performance. The process has no intrinsic scaleup limitations, so substrates of nearly any size can be coated.

One of our applications involves high reflectors (HRs) used in large-aperture, high-power laser systems. Traditional HRs are deposited by electron-beam evaporation in vacuum. Sol-gel multilayer HRs offer a low-cost, low-coating-stress alternative to traditional HRs. For example, we expect to use sol-gel HRs as cavity end mirrors for the proposed National Ignition Facility (NIF), a 192-beam megajoule-class glass laser based on a multipass amplifier architecture.

A sol-gel multilayer HR consists of alternating layers of oxide particles of high and low refractive index deposited on a substrate. Optical interference effects at the interfaces between layers cause nearly complete reflection at a desired wavelength of light, while allowing other wavelengths to be transmitted. For our application, layer thicknesses of 0.1 to 0.2  $\mu\text{m}$  are typical, and up to 30 layers are required to achieve high reflectivity in a multilayer stack.



Working with a company specializing in industrial coating machines, we have designed, built, and fielded an automated meniscus coating machine, a prototype for the machines needed to make the numerous HRs required for the NIF. The machine has been used to make a demonstration HR on the Beamlet laser, a prototype for the NIF design. This 38- × 38-cm HR contains 13 coatings of porous silica alternating with 13 layers of zirconia with a polyvinylpyrrolidone binder. The mirror has an average transmission of 1.57% with a standard deviation of 0.16%.

Large-area diffraction gratings are another important application. The technique of chirped-pulse amplification uses diffraction gratings to expand subpicosecond laser pulses in time and then to recompress them after amplification. This technique is allowing researchers to develop new laser systems that can deliver power levels of more than one terawatt ( $10^{12}$  W). Such power levels offer exciting opportunities for studying the interaction of light and matter and for investigating fusion power.

The internally funded petawatt project at LLNL will convert one of the ten beams of the Nova laser into an independent laser capable of delivering a petawatt ( $10^{15}$  W) of power in a 1-picosecond pulse. The pulse-

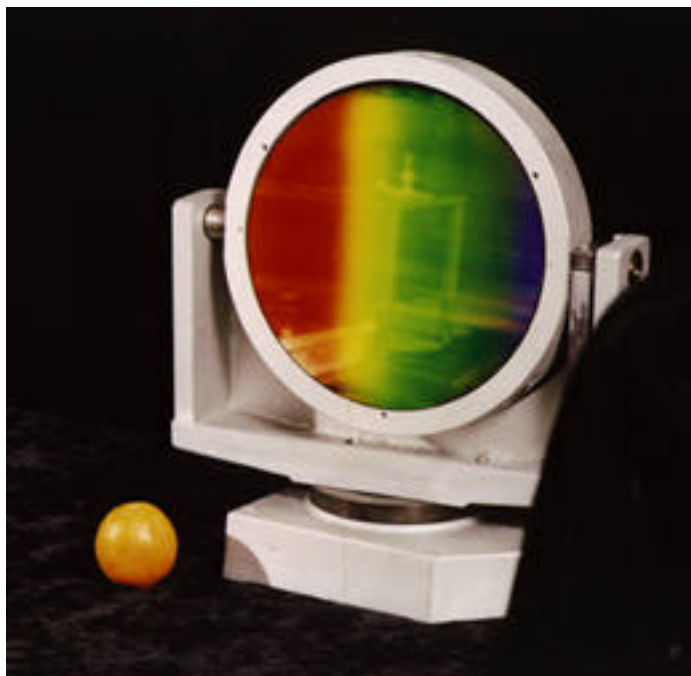
compression gratings in the Petawatt laser will be approximately  $100 \times 60$  cm in size. Gratings this large can only be made by holographic techniques. A photoresist film on the substrate is exposed to the interference pattern resulting from the intersection of two highly collimated (nearly parallel) ultraviolet laser beams, and the exposed pattern in the resist is developed. The grating structure in photoresist is then overcoated with a metal layer (usually gold) to make a high-efficiency reflective grating.

We have created high-efficiency gratings by applying the photoresist film at the thickness corresponding to the line height that maximizes grating efficiency. We then process the optic so that the exposed photoresist dissolves down to the substrate, whereas the unexposed resist remains at nearly the original film thickness.

We have used our meniscus coating procedure to make several 30-cm-diameter gratings (photo below). These gratings exhibit 94% absolute diffraction efficiency for 1.06- $\mu$ m light. We have also made several 15- and 30-cm-diameter gratings of similar quality for pulse compression of 825-nm light. Our next challenge is to make the large gratings for the Petawatt laser.

Flat panel displays are a promising new application with a huge potential market. These devices present a challenge to current processing technologies from both cost and performance standpoints. At present, their processing involves spin coating photoresist and color filter layers onto glass panels, a procedure borrowed from integrated-circuit manufacturing. Such processing is both unwieldy and expensive because the coating fluids cost several hundred dollars per liter, and about 99.5% of the applied liquid is flung off the substrate during the high-rpm process. Edge nonuniformities in film thickness are also plainly visible on large rectangular or square spin-coated glass panels.

We have demonstrated that meniscus coating can provide adequate coating uniformity and reproducibility for flat panel display processing, along with nearly 100% utilization of coating fluids. We are confident that our technology has a bright future in this new application.



*One of our new 30-cm-diameter diffraction gratings used for pulse compression of high-power lasers. This grating, with 1740 lines per millimeter, exhibits 94% absolute diffraction efficiency for 1.06- $\mu$ m light, and it has a wavefront flatness of less than one-fifth wave over the usable aperture.*

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